Environmental Pollution xxx (2018) 1–10

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

The occurrence of brominated flame retardants in the atmosphere of Gauteng Province, South Africa using polyurethane foam passive air samplers and assessment of human exposure☆

Zainab J. Katima [a, b], Olubiyi I. Olukunle [c], Olga-loanna Kalantzi [d], Adegbenro P. Daso [a], Jonathan O. Okonkwo [a, *]

[a] Environmental Chemistry Research Group, Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa
[b] University of Dar es Salaam, College of Engineering and Technology, Department of Chemical and Mining Engineering, P.O. Box 35131, Dar es Salaam, Tanzania
[c] School of Public and Environmental Affairs, Indiana University, 702N Walnut Grove Avenue, Bloomington, 47405, Indiana, USA
[d] Department of Environment, University of the Aegean, Mytilene, 81100, Greece

ARTICLE INFO

Article history:
Received 28 May 2018
Received in revised form
12 July 2018
Accepted 17 July 2018
Available online xxx

Keywords:
Brominated flame retardants
Atmosphere
PUF
Human exposure
South Africa

ABSTRACT

Polyurethane foam passive samplers were deployed between May 2016 and January 2017 to evaluate concentrations of polybrominated diphenyl ethers (PBDEs), selected alternative flame retardants (AFRs) and total hexabromocyclododecane (HBCDD) (sum of α-, β-, and γ-HBCDD). The PUF air samplers were deployed in semi–urban, urban, industrial and landfill sites in Gauteng Province, South Africa. The acquired results presented a clear semi urban–industrial–urban–landfill concentration gradient for all BFRs measured. Taking into account 2 sampling periods (cold and warm periods) ($n = 16$), the atmospheric concentrations of $\sum_9$PBDEs, HBCDDs and $\sum$AFRs were 100–2820 pg m^{-3}, 12–117 pg m^{-3} and 41–4660 pg m^{-3}, respectively, for the sparsely populated residential area, densely populated residential area, industrial area and the landfill area. In all cases, BDE 47, 99, and 209 were the most dominant congeners with high detection frequencies. The highest calculated daily exposure dose in Gauteng Province atmosphere was 0.61 and 1.54 ng kg^{-1} – bw d^{-1} for adults and children respectively. The estimated total intake of PBDEs was 0.47–33.4 ng kg^{-1} – bw d^{-1}, which was generally below the lowest adverse effect limit (LOAEL), suggesting that the residents of Gauteng Province may not be significantly affected as a result of their exposure to these pollutants through inhalation. However, this does not necessarily suggest that the pollutants are harmless to human health, since they have the tendency to bioaccumulate in biological systems. Incidentally, this is the first study from Africa to report on the atmospheric concentrations of PBDEs, HBCDDs and AFRs in urban, landfill and industrial areas. The findings from this study further highlight the contributory role of landfills as potential sources of BFRs into the atmosphere.

1. Introduction

Brominated flame retardants (BFRs) are bromine-containing organic chemicals that are deliberately added into materials to inhibit their combustion rates thereby reducing the spread of fire and fire related damages and deaths (Besis et al., 2017). The aforementioned group of compounds have been incorporated into a variety of consumer products such as upholstered furniture, electronic devices and curtains since the 1970s (Kalantzi & Siskos, 2011; Qi et al., 2014). There are two classes of BFRs frequently documented in studies and these are, legacy BFRs including PBDEs, tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCDDs); and those referred to as alternative FRs (AFRs) such as decabromodiphenyl ethane or 1,2-bis(pentabromodiphenyl) ethane (DBDPE), hexachlorocyclopentadienyldibromo-cyclooctane (HCDBCO), tetrabromobisphenol A-bis(2,3-dibromopropylether) (TBBPA-DBPE), bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate

☆ This paper has been recommended for acceptance by Charles Wong.
* Corresponding author.
E-mail address: OkonkwoOJ@tut.ac.za (J.O. Okonkwo).

https://doi.org/10.1016/j.envpol.2018.07.075
0269-7491/

(TBPH or BEH-TBP), 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), amongst others (Covaci et al., 2011). Literature has shown that some BFRs possess similar properties to known persistent organic pollutants (POPs). Certain persistent organic pollutants are known to undergo long-range atmospheric transport, bio-accumulate, and have the ability to cause potential adverse effects on living organisms (Ali et al., 2011). In fact, some animal studies have also shown that PBDEs, HBCDDs and AFRs can affect the liver, thyroid and reproductive systems which could lead to neurochemical and hormonal dysfunction (Akortia et al., 2016; Kurt-karakus et al., 2017; Legler & Brouwer, 2003; Ni & Zeng, 2013; De la torre et al., 2018). Consequently, the major congeners of the commercial formulations of PentaBDE and OctaBDE were listed under the Stockholm Convention on persistent organic pollutants (POPs) in 2009. Recently, DecaBDE has also been added to the POPs list due to concerns related to its possible degradation to lower brominated congeners that are more toxic and persistent in the environment (UNEP, 2017). Despite the global restrictions on the manufacture of certain PBDEs, particularly in most developed countries, they are still being detected at elevated levels in different environmental matrices (Bjermo et al., 2017; Morris et al., 2018; Parry et al., 2018; Zhihua et al., 2018).

With respect to the atmospheric burdens of most BFRs, particularly PBDEs, HBCDDs, TBBPA and AFRs, there is still paucity of information in the entire southern hemisphere. This presents a challenge to understanding the regional perspective of these pollutants in the atmosphere. In the African continent, only three studies have been conducted so far on atmospheric levels of BFRs, and these were mainly focused in background areas (Katima et al., 2017).

There is no record of BFRs production in any African country and, therefore, the only possible source of these pollutants entering the waste stream is assumed to be through imported consumer products, such as computers, electrical and electronic appliances, furniture, carpets and mattresses, amongst others.

Previous studies in South Africa have reported the occurrence of PBDEs, HBCDDs and AFRs in different environmental matrices such as indoor air and dust from selected sites (Abafe & Martincigh, 2015; Kefeni & Okonkwo, 2012; Kefeni et al., 2014; Nkabinde et al., 2018), atmosphere (Pozo et al., 2008), landfill leachate (Daso et al., 2013; Odusanya et al., 2009; Olukunle & Okonkwo, 2015), water and sediments (La guardia et al., 2013; Olukunle et al., 2012; Olukunle & Okonkwo, 2015), sewage sludge and wastewater effluent (Daso et al., 2012), human breast milk (Darnerud et al., 2011), and bird eggs (Daso et al., 2015; Polder et al., 2008). These reports demonstrate the presence of BFRs in the South African environment. However, there are no published studies in Africa including South Africa on the levels and sources of atmospheric BFRs in the urban, industrial as well as landfill areas (Katima et al., 2017).

Hence, the objectives of this study were first and foremost, to measure the atmospheric concentrations of PBDEs, HBCDDs and selected AFRs in Gauteng Province, South Africa, using passive air samplers. Secondly, to evaluate the human exposure risk associated to these pollutants in the atmosphere as well as to establish the affected receptor countries at higher pollutant concentrations. To our knowledge, this is the first study from the African continent to report atmospheric concentrations of PBDEs, HBCDDs and AFRs in landfills and industrial areas.

2. Materials and methods

2.1. Study area

Gauteng is the smallest province in South Africa occupying roughly 1.4% of the land with an area of 16,936 km^2. However, it is the most populous province in the country with a population of approximately 13.4 million people, representing 24.1% of the country's population. The province consists of the country's administrative capital (Pretoria), the largest city (Johannesburg) and other large industrial suburbs such as Midrand and Vanderbijlpark. The climate in Gauteng is comparatively cool, despite the fact that it has a subtropical climate. Precipitation frequently befalls as brief afternoon thunderstorms. The warmest climate is in January with average temperatures between 15 °C and 29 °C, while the coldest climate is in June with average temperatures between 4 °C and 16 °C. The annual precipitation is between 674 and

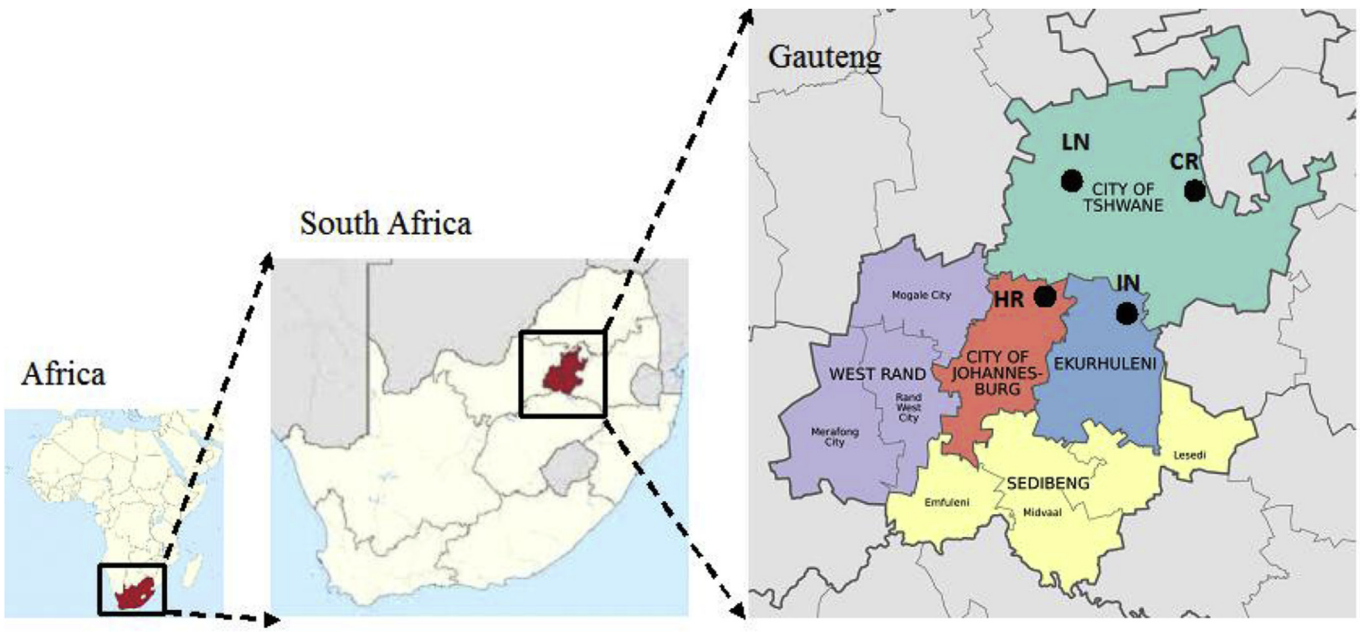

Fig. 1. Maps showing the location of Gauteng Province as well as the sampling points.

Please cite this article in press as: Katima, Z.J., et al., The occurrence of brominated flame retardants in the atmosphere of Gauteng Province, South Africa using polyurethane foam passive air samplers and assessment of human exposure, Environmental Pollution (2018), https://doi.org/10.1016/j.envpol.2018.07.075